

# Airborne Arsenic and Urinary Excretion of Arsenic Metabolites during Boiler Cleaning Operations in a Slovak Coal-fired Power Plant

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Little information is available on the relationship between occupational exposure to inorganic arsenic in coal fly ash and urinary excretion of arsenic metabolites. This study was undertaken in a coal-fired power plant in Slovakia during a routine maintenance outage. Arsenic was measured in the breathing zone of workers during 5 consecutive workdays, and urine samples were obtained for analysis of arsenic metabolites—inorganic arsenic ( $\text{As}_3$ ), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA)—prior to the start of each shift. Results from a small number of cascade impactor air samples indicated that approximately 90% of total particle mass and arsenic was present in particle size fractions  $\geq 3.5 \mu\text{m}$ . The 8-hr time-weighted average (TWA) mean arsenic air concentration was  $48.3 \mu\text{g}/\text{m}^3$  (range 0.17–375.2) and the mean sum of urinary arsenic ( $\Sigma\text{As}$ ) metabolites was  $16.9 \mu\text{g As/g creatinine}$  (range 2.6–50.8). For an 8-hr TWA of  $10 \mu\text{g}/\text{m}^3$  arsenic from coal fly ash, the predicted mean concentration of the  $\Sigma\text{As}$  urinary metabolites was  $13.2 \mu\text{g As/g creatinine}$  [95% confidence interval (CI), 10.1–16.3]. Comparisons with previously published studies of exposure to arsenic trioxide vapors and dusts in copper smelters suggest that bioavailability of arsenic from airborne coal fly ash (as indicated by urinary excretion) is about one-third that seen in smelters and similar settings. Arsenic compound characteristics, matrix composition, and particle size distribution probably play major roles in determining actual uptake of airborne arsenic. **Key words:** arsenic, biological monitoring, coal, occupational exposure, power plant, urinary metabolites. *Environ Health Perspect* 105:836–842 (1997)

<http://ehp.niehs.nih.gov>

Occupational exposure to arsenic is known to occur in a number of work settings including arsenic pesticide manufacturing and use, arsenic refining, glassware factories, semiconductor fabrication, and nonferrous smelters (1,2). Arsenic is considered a human carcinogen based principally on results from epidemiological studies that include investigations of occupational exposure as well as ecological studies of exposure to naturally occurring arsenic in drinking water (3). Occupational epidemiological studies have been conducted principally in copper smelting operations wherein past high airborne exposures have been associated with increased risk of lung cancer (4–11). Similarly, most occupational studies to date relating arsenic air exposure to urinary excretion have been conducted in nonferrous smelters (12–17). It is of interest to examine other work settings to assess potential impacts of differences in exposure parameters. For example, differences in arsenic compound(s), physical form(s), and matrix compositions in different work settings may lead to differences in arsenic uptake as estimated by the relationship between air monitoring and urinary excretion (18).

Coal used in U.S. power plants is known to contain trace amounts of arsenic with averages ranging from 2 to 24 ppm. Coal-fired power plant boilers are routinely shut down at about 1-year intervals for cleaning

and maintenance operations; such events are termed planned maintenance outages. Activities during these operations present opportunities for elevated fly ash exposures relative to the usual exposure circumstances during routine work tasks performed during normal operations of a coal-fired power plant. The purpose of this study was to assess occupational exposure to arsenic in coal fly ash dust during maintenance outage operations in a coal-burning power plant that has previously been identified as utilizing coal containing very high arsenic levels.

## Material and Methods

**Power plant.** The coal-fired power plant at which the study was carried out is located near the town of Novaky in the central Slovak Republic. The plant, referred to as Novaky ENO, has been in operation since 1953; local low-grade brown lignite coal containing a mean concentration of approximately 800 ppm arsenic (maximum 1350 ppm) is the principal fuel used at this plant (19). In comparison with coals used in U.S. coal-fired power plants, Slovak lignite coal contains on the average about 30–300 times higher arsenic concentrations. The first boiler unit of the plant began operation in 1953 with 180 megawatt (MW) output capacity. A second 220 MW unit began operating in 1964 and, in 1979, a third 220 MW unit was built. Technological improvements, as

well as reduction of the total output from 620 MW to 250 MW, has resulted in a reduction of arsenic emissions to ambient air from 90 tons of arsenic emitted per year in 1980 to 2.7 tons emitted in 1993 (19).

Work activities during the maintenance outage studied at this coal-fired power plant were very similar to those observed in coal-fired power plants in the United States (20). During the initial stages of a maintenance outage, work activities are routinely directed toward removal of accumulated fly ash and clinker from inside the boiler structure as well as the electrostatic precipitators (ESPs) by use of vacuum systems and manual methods later followed by manual wet methods. Maintenance and repair inside the boiler is often performed in and around residual fly ash that is not completely removed, and this ash becomes airborne when agitated.

**Subjects.** Workers were initially interviewed to determine interest in study participation and general health background. Forty healthy power plant workers participated in the study with informed consent. Work categories were selected to obtain observations over as wide a gradient of exposure as possible. Worker groups boilercleaner and boiler-maker differ in duties in that boilercleaners are involved exclusively in cleaning activities inside the boiler and other interior spaces of the boiler structure such as ESPs, whereas boilermakers are involved in general repair and maintenance of equipment that may be located either inside the boiler or in other areas around the boiler. The technician category consisted of other workers involved in plant operations that were not necessarily involved in the outage activities. This group included electricians, technicians, operators, and stokers and those engaged in general

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The authors gratefully acknowledge the outstanding contributions of the field and laboratory research teams at the Specialized State Health Institute, Banska Bystrica, and the State Health Institute, Prievidza, The Slovak Republic. Many thanks also for excellent statistical support to Mark Segal and Margaret Wrench, University of California, San Francisco and consultant Abe Silvers. This study was supported by the Electric Power Research Institute under contract WO 3370-12 Specialized State Health Institute and WO 3370-20 Geomatrix Consultants, Inc.

Received 27 December 1996; accepted 3 April 1997.

maintenance and workshop activities in operational areas of the plant. Twenty community referents also volunteered to participate. A questionnaire was administered to all subjects to obtain information on work history, diet (including consumption of seafood in the week preceding the start of the study), smoking, alcohol intake, medical history, and other lifestyle factors.

**Air sampling.** Time-integrated full shift air samples were collected in the breathing zone of each worker during each of the 5 consecutive days of the work week. For daily personal samples, battery-powered personal air sampling pumps (SKC Model 224-PCXR3; SKC, Fullerton, CA) were coupled with matched weight 37-mm mixed cellulose ester filters housed in two-stage plastic cassettes (SKC 225-503) according to standard methods (21,22). Air samples were collected at a flow rate of 2.0 lpm; air flow rates were calibrated at the beginning, during, and at the end of the sampling time by use of a precision rotameter (SKC 320-4A5), which had been calibrated against a soap film calibration device (Amatec Prime Air calibrator; Amatec, Orlando, FL) each day prior to the initiation of field sampling. Filter cassettes were carefully inspected during the entire sampling period for potential overloading. Occasionally it was necessary to replace the sample filter cassette; in this event, results from analysis of both filters were combined to calculate the 8-hr time-weighted average (TWA) concentration. Gravimetric and arsenic analyses were carried out on each filter as described below.

A small number of airborne particle size distribution samples were collected by use of a battery-powered personal air sampling pump (Gilian Model HFS 113A; Gilian, West Caldwell, NJ) connected to a six-stage personal cascade impactor (Marple Model 296; Graseby, Atlanta, GA). Three personal samples were collected in the breathing zone of workers, and four area samples were collected by suspending the device approximately 5 ft in height from a tripod placed in selected work stations. Area sampling was performed in locations where it was impossible for the worker to wear sampling equipment due to a constrained work area (usually inside the boiler). Cascade impactor filters were desiccated and weighed on a microbalance prior to sampling. Gravimetric and arsenic analyses were carried out on each filter as described below.

**Analysis of air samples.** For the gravimetric method for total dust, two matched-weight filters were weighed on a six-place microbalance (Cahn Instruments, Philadelphia, PA) following a 48-hr desiccation period. Filters were weighed within

0.01 mg. Differences between the matched-weight filters were calculated and results were expressed as total mass of particulate (milligram) per cubic meter of air. Quality control included daily instrument calibration with standard weights replicate analysis and analysis of field blanks, which constituted approximately 10% of samples.

For the analysis of arsenic, filters containing collected particulate were digested according to National Institute for Occupational Safety and Health (NIOSH) Method 7900 (22) in closed Teflon beakers. Analysis was conducted using graphite furnace-atomic absorption spectrometry [Varian Spectre Model AA-30 (Varian, Palo Alto, CA) with GTA-96 graphite tube atomizer]. Daily analytical quality control procedures consisted of analysis of three separate reagent blanks and instrument calibration at three different known arsenic concentrations. Weekly quality control analyses for arsenic were carried out on the National Bureau of Standards (NBS) Trace Elements in Coal Fly Ash, 1633a, Standard Reference Material (SRM) sample. Results of these analyses ( $n = 19$ ) showed a mean arsenic recovery of 110% (range 91.5–145) of the target concentration in the SRM coal fly ash. Replicate analyses of 10% of all samples was also carried out on a weekly basis.

**Daily work activity diary.** A daily diary of work activities was completed by a member of the research team for each worker based on brief employee interviews throughout the day and observations made in the workplace. Information included time of day, work location, work activities, and respirator usage. Standard respirators at this plant consisted of washable fabric dust masks held in place by tie strings.

**Urine sampling.** Preshift spot urine samples were collected at home prior to the work shift on each of 5 consecutive working days for each individual. Urine was collected in clean containers provided by the laboratory. Urine samples were also collected from community volunteers not employed at the power plant on two consecutive mornings chosen randomly over the period during which the occupational study was carried out.

**Urine analysis.** Creatinine concentration in urine samples was determined using the Jaffe method (23). Arsenic species consisting of inorganic arsenic ( $As_i$ ), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) were quantified in urine by the hydride generation method coupled with atomic absorption spectrometry (24–27). Briefly,  $As_i$ , MMA, and DMA were volatilized from solution after reduction to the corresponding arsines with sodium borohydride. Volatilized arsines were then introduced onto a liquid

nitrogen-cooled Chromosorb PAW-DMCS (3% OV 101) chromatographic trap (VWR Co., Chicago, IL), which, upon warming, allowed for separation of species based on boiling points. The released arsines were carried by helium into a quartz cuvette burner cell where they decomposed to atomic arsenic. Arsenic concentrations were then determined by atomic absorption spectroscopy. Daily quality control procedures included triplicate blank reagent analyses; daily calibration checks using three different known concentrations of standard solutions of  $As_i$ , MMA, and DMA; and daily spiked urine samples containing standard addition quantities of known arsenic species. Analytical results from spiked urine species yielded mean arsenic species percent recoveries and coefficients of variation (CV) as follows: for  $As_i$ , 105% recovery and CV 22%; for MMA, 104% recovery and CV 20%; and for DMA, 137% recovery and CV 31%. Additionally, results of weekly analysis of the NBS SRM 2670 standard urine sample, Toxic Metals in Freeze Dried Urine, showed a mean recovery of 105.4% (range 80–143) with a CV of 26.5%. Approximately 10% of all samples were water blanks, and 10% of all samples were analyzed twice as a precision check. Overall precision averaged 4% for  $As_i$ , 8% for MMA, and 13% for DMA. Analytic results from this laboratory also compared favorably with other participating laboratories in a concurrently conducted interlaboratory comparison study (28).

**Statistical methods.** Grouped data were analyzed using standard parametric methods. Supplementary analyses were carried out on individual log transformed data using univariate and multivariate linear mixed models (29) to assess the impact of adjustment for nonindependence of urinary values resulting from repeated measures on each worker as well as other selected variables. Models were fitted using the SAS statistical software package (SAS Institute, Cary, NC) (30).  $p < 0.05$  was selected as the critical value for statistical significance for all statistical tests.

**Table 1.** Selected characteristics of study participants

Group	Age in years (years $\pm$ SD)	Number of smokers	Number eating seafood
Boilercleaners ( $n = 9$ )	40.1 $\pm$ 1.6	5	0
Boilermakers ( $n = 13$ )	32.5 $\pm$ 2.6	7	0
Technicians ( $n = 18$ )	38.6 $\pm$ 2.3	7	2
Community referents ( $n = 20$ )	38.8 $\pm$ 6.2	13	1

SD, standard deviation.

**Table 2.** Airborne arsenic exposure, total airborne dust exposure, and concentrations of arsenic species in urine as shown by geometric mean and geometric standard deviation

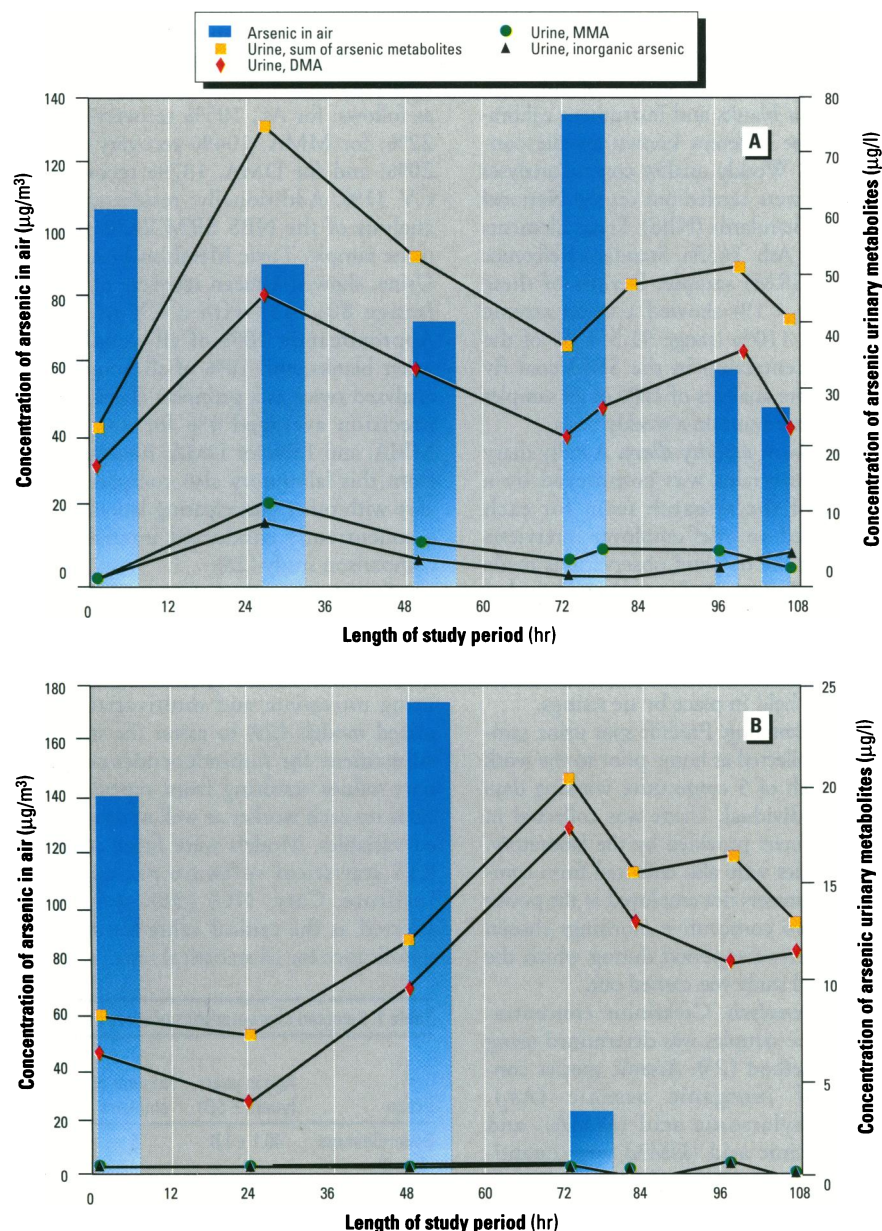
Group	Arsenic in air ( $\mu\text{g}/\text{m}^3$ )	Dust in air ( $\text{mg}/\text{m}^3$ )	Arsenic species in urine ( $\mu\text{g As/g creatinine}$ )			
			As <sub>i</sub>	MMA	DMA	$\Sigma\text{As species}$
Boilercleaners <sup>a*</sup> ( <i>n</i> = 9)	$59.5 \pm 1.3$	$19.1 \pm 1.3$	$4.2 \pm 1.1$	$4.3 \pm 1.1$	$12.7 \pm 1.1$	$22.1 \pm 1.1$
Boilermakers ( <i>n</i> = 13)	$17.2 \pm 1.3$	$4.4 \pm 1.2$	$2.8 \pm 1.2$	$2.3 \pm 1.1$	$7.1 \pm 1.2$	$13.4 \pm 1.1$
Technicians <sup>b</sup> ( <i>n</i> = 18)	$2.1 \pm 1.2$	$1.3 \pm 1.2$	$3.0 \pm 1.1$	$1.9 \pm 1.1$	$5.5 \pm 1.1$	$11.4 \pm 1.1$

$\Sigma\text{As species}$ , sum of As species.

<sup>a</sup>Includes two scaffold workers.

<sup>b</sup>Includes maintenance workers, electricians, operators, and stokers.

\*Significantly different from boilermakers and technicians (ANOVA,  $p = 0.002$ ).

**Figure 1.** Arsenic air exposure measurements and patterns of individual urinary metabolite excretion plotted over the entire time period of the study for two randomly chosen workers, (A) Worker 4 and (B) Worker 28. These data illustrate the study design and nature of the data collected. DMA, dimethylarsinic acid; MMA, monomethylarsonic acid.

## Results

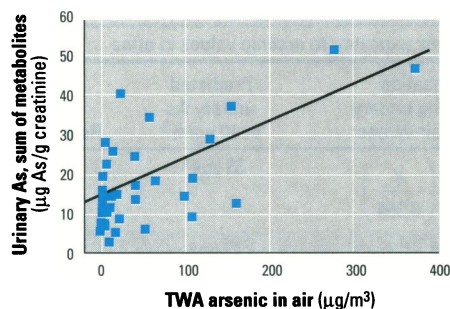
Table 1 provides descriptive information for each worker group on age, smoking, and seafood consumption during the week prior to the study period. No seafood was consumed by the more highly exposed groups and very little was consumed by either the low exposed group or community referents. Data collected from the questionnaire indicated that approximately 10% of study participants used local coal for home heating. Examination of community referent data, however, showed no correlation between home coal use and urinary values. Because the study was conducted in mid-summer, active home heating was probably not used in any of these households during the study period.

Individual values for arsenic air concentrations and urinary arsenic metabolite concentrations were distributed log-normally. Six individual urine samples that were considered either too dilute or too concentrated (creatinine concentrations  $<0.3 \text{ g/l}$  or  $>3 \text{ g/l}$ ) were not included in the analysis. Table 2 lists the geometric mean (GM) and geometric standard deviation (GSD) of exposure to arsenic and dust, as well as arsenic metabolite urinary excretion values, for each of the worker groups. Daily exposures to total dust and arsenic concentrations were higher during the first few days of the outage, when manual dry cleaning methods were employed, and then rapidly fell later in the first and second week, as wet methods were used (data not shown).

Analysis of variance (ANOVA) showed a significant difference between the boilercleaner group GM air arsenic values and GM sum of arsenic metabolite species ( $\Sigma\text{As}$  metabolites) and the boilermaker and technician groups ( $p = 0.002$ ). However, air and urinary values were not significantly different between the latter two groups themselves ( $p = 0.467$ ). No significant difference was found among any of the three groups for GM urinary As<sub>i</sub> values ( $p = 0.186$ ). Arithmetic means for air arsenic values were as follows: boilercleaners,  $138.9 \mu\text{g}/\text{m}^3$ ; boilermakers,  $67.7 \mu\text{g}/\text{m}^3$ ; technicians,  $5.7 \mu\text{g}/\text{m}^3$ . Arithmetic means for  $\Sigma\text{As}$  urinary metabolites for each group were boilercleaners,  $25.7 \mu\text{g As/g creatinine}$ ; boilermakers,  $17.8 \mu\text{g As/g creatinine}$ ; and technicians,  $13.3 \mu\text{g As/g creatinine}$ . The mean  $\Sigma\text{As}$  urinary metabolites value for community referents ( $n = 20$ ) in first void urine samples collected on two randomly selected consecutive days during the study period was  $9.2 \mu\text{g As/g creatinine}$ .

Air arsenic exposure and concentrations of arsenic species in urine were plotted for every subject against the time point that the measurements were obtained for the entire length of the study period. Figure 1





**Figure 2.** Plot of mean time-weighted average (TWA) arsenic air concentration versus mean sum of arsenic metabolites excreted during 5 days ( $n = 40$ ;  $r = 0.67$ ).

illustrates two such individual worker plots. Inspection of plots revealed high interindividual variability in both exposure and urinary metabolite excretion patterns. Inspection of urinary  $\Sigma$ As metabolite values for worker samples collected prior to the start of the first shift also showed variability (mean  $10.83 \mu\text{g As/g creatinine} \pm 6.0$ ; range  $1.9\text{--}28.1$ ). Comparison of workers' mean first morning urinary values (zero hour on Fig. 1) with community referents values showed no significant difference [ $10.8$  vs.  $9.2 \mu\text{g As/g creatinine}$ ;  $t$ -test (two-tailed),  $p = 0.13$ ]. Higher individual values within the worker group implied that some workers may have been occupationally exposed to arsenic during the week preceding the study period.

Regression of mean air arsenic values ( $x$ ) for each worker during the study period on mean  $\Sigma$ As metabolites in urine ( $y$ ) 16 hr postshift (excluding urinary values for the preshift sample on the first morning) was statistically significant ( $n = 40$ ;  $y = 12.22 + 0.10 x$ ;  $p < 0.001$ ;  $r = 0.67$ ) (Figure 2). Analyses were run with and without inclusion of percent daily time recorded wearing a cloth dust mask respirator; no discernible effect on regression of inclusion of the variable for respirator usage was noted; therefore, final analyses excluded this variable. Removal of the two highest points from regression had no effect on regression. Using the above equation, for an 8-hr TWA air arsenic value of  $10 \mu\text{g/m}^3$ , the predicted  $\Sigma$ As urinary metabolites was  $13.2 \mu\text{g As/g creatinine}$  [95% confidence interval (CI),  $10.1\text{--}16.3$ ].

To investigate the potential impact of interindividual variability on the exposure-response relationship, analyses were carried out using individual pairs (TWA air concentration vs. urine value 16 hr postshift) of observations for each subject. Log air arsenic versus log urinary metabolite data were examined for each metabolite and for the  $\Sigma$ As metabolites ( $n = 123$ ) utilizing univariate and multivariate linear mixed models in SAS. This approach allowed

**Table 3.** Arsenic and dust concentration and percent particle mass per cascade impactor stage<sup>a</sup>

Stage	Stage cut-point ( $\mu\text{m}$ )	Particle mass <sup>b</sup> (%)	Dust <sup>b</sup> ( $\text{mg/m}^3$ )	Arsenic <sup>b</sup> ( $\mu\text{g/m}^3$ )
Back-up	0.25–0.5	$1.8 \pm 1.6$	$0.8 \pm 0.6$	$1.5 \pm 1.8$
8	0.5–0.9	$1.3 \pm 0.8$	$0.7 \pm 0.3$	$0.7 \pm 0.8$
7	0.9–2.0	$1.9 \pm 1.4$	$1.0 \pm 0.3$	$0.9 \pm 0.6$
6	2.0–3.5	$2.4 \pm 1.0$	$1.4 \pm 0.7$	$5.8 \pm 3.9$
5	3.5–6	$12.1 \pm 5.1$	$8.1 \pm 5.6$	$13.7 \pm 7.5$
4	6–10	$32.5 \pm 10.6$	$21.2 \pm 13.1$	$33.6 \pm 15.0$
3	>10	$47.9 \pm 17.5$	$35.3 \pm 26.9$	$66.3 \pm 58.1$

<sup>a</sup>Mean of seven cascade impactor samples including three personal samples and four work area samples.

<sup>b</sup>Values shown are mean  $\pm$  standard deviation.

adjustment for between-individual variation in initial urinary arsenic levels and also for statistical dependence induced by making repeated measurements per worker. The potential impact of serial dependence was explored; however, model comparison statistics revealed this to be unnecessary. Regression terms (fixed effects) for week, day of week, and work group, as well as log air arsenic concentration, were included in multivariate models to affect adjustment for these variables. Interaction between log air arsenic and week or day was investigated; however, no significant interactions were identified. Models were run on each urinary metabolite individually as well as on the  $\Sigma$ As metabolites. Multivariate regression models indicated that urinary MMA ( $\log y = -0.005 + 0.071 \log x$ ), DMA ( $\log y = 0.488 + 0.101 \log x$ ), and  $\Sigma$ As metabolites ( $\log y = 0.430 + 0.058 \log x$ ), but not  $\text{As}_i$  values ( $\log y = 0.063 + 0.031 \log x$ ), were significantly ( $p < 0.05$ ) related to arsenic air exposure after statistical adjustment as described.

The group mean MMA:DMA ratio for the most highly exposed group, boiler-cleaners ( $0.34 \pm 0.16$ ), was not found to be significantly different from that of the lowest exposure group, technicians ( $0.36 \pm 0.18$ ;  $t$ -test,  $p = 0.62$ ).

Results from the seven cascade impactor samples are shown in Table 3. Approximately 90% of particle mass (and 93% of arsenic) was present in fractions  $\geq 3.5 \mu\text{m}$  aerodynamic diameter. Ratios of micrograms of As per cubic meter to milligrams of dust per cubic meter for each impactor stage indicate that arsenic was distributed fairly uniformly across all particle size fractions because no significant difference was found among ratios for different impactor stages ( $\chi^2 = 3.71$ ,  $p = 0.72$ ).

## Discussion

Work activities during the maintenance outage studied at this coal-fired power plant were very similar to those observed in coal-fired power plants in the United States (20). The local brown lignite coal used as the fuel source in the Novaky power plant

is, however, very dissimilar to coal burned in U.S. power plants, particularly with regard to arsenic concentration. Slovak lignite coal contains a mean of 800 ppm arsenic and ranging up to 1350 ppm (19). U.S. coals, on the other hand, contain considerably less arsenic; bituminous coal contains the highest amounts of arsenic among U.S. coals, with a mean of 23.5 ppm arsenic (31). The other major types of U.S. coal contain even less arsenic (subbituminous coal contains 2.7 ppm arsenic on average while lignite coal contains an average of 5.0 ppm arsenic). Bituminous and subbituminous coals are the two most commonly burned coals in U.S. power plants (32). Conventional coal cleaning procedures employed in the United States prior to burning coal result in an average 50% further reduction in arsenic content below levels listed above (33).

Urinary data 16 hr postshift were related to air arsenic concentrations using grouped information (i.e.,  $n = 40$  pairs of mean urinary values and mean personal exposure values averaged over the study period of 5 days) as well as individual log urine and log air sample results for each worker for each day ( $n = 123$ ). As previously mentioned, these multivariate analyses were undertaken to explore the potential effect on regression of repeated measures and other factors. Predicted  $\Sigma$ As urinary values for a fixed air arsenic exposure of  $10 \mu\text{g/m}^3$ , based on the grouped and individual approaches that both employ linear models, were in quite good agreement ( $13.2$  and  $9.8 \mu\text{g As/g creatinine}$ , respectively). Seixas and Sheppard (34) compared accuracy and precision using either grouped or individual exposure measurements; they found that predictions based on a linear approach with grouped data appeared to be most robust. Because the majority of occupational studies on arsenic air exposure and urinary excretion have taken a similar approach in data grouping and analysis, comparability of results is facilitated by using this method.

During the past 20 years, at least five studies have been undertaken in copper

smelters and arsenic trioxide refineries in which individual breathing zone exposure to arsenic vapors and dusts and urinary arsenic concentrations were measured (12–15,17). Area measurements were used in another copper smelter study to estimate past personal exposure; these grouped exposure estimates were then related to grouped urinary excretion of arsenic species (8). Other studies of arsenic exposure have also been conducted: in a lead–acid storage battery factory where exposure to arsine gas and arsenic dust occurred (35), in a sulfuric acid chemical factory where exposure to arsenic trioxide vapors and dust were measured (16), and in a glass manufacturing plant where exposure to arsenic trioxide was assessed (36).

Summary information for seven studies in which the mathematical relationship between air exposure and urinary excretion was determined by the authors is shown in Table 4, along with results from this present study. In one instance, the equation was estimated from data presented in the paper (13). Whenever data were available, equations in the table represent the relationship between air and urine values (as  $\Sigma$ As metabolites or, in three instances, as total arsenic) in samples collected 16 hr postexposure. Using these equations (Table 4), the estimated predicted value of arsenic in urine (either as total As or the  $\Sigma$ As metabolites), given a mean 8-hr TWA arsenic air value of 10  $\mu\text{g}/\text{m}^3$  was calculated. Urinary values are listed in the same units (micrograms As per liter or micrograms As per gram creatinine) as used by the original authors.

There is remarkably good agreement among the first seven studies listed in Table 4 in terms of predicted concentration of urinary arsenic at 10  $\mu\text{g}/\text{m}^3$  arsenic exposure. Three of the studies (8,12,35) measured only total arsenic in urine; no speciation data on metabolites are available for these studies. Five studies were conducted in copper smelters where exposure to arsenic trioxide dust and vapors occurred (Table 4). The remaining two studies listed are a study of exposure to arsine gas in a lead–acid battery factory (35) and a study of exposure to arsenic trioxide fumes and dust in a sulfuric acid chemical factory (16). Assuming a urinary creatinine concentration of 1.13 g/l, the overall average predicted value for arsenic in urine from these studies at 10  $\mu\text{g}/\text{m}^3$  arsenic in air is 33.4  $\mu\text{g}/\text{g}$  creatinine  $\pm$  8.7 (mean  $\pm$  SD).

In the study by Enterline et al. (8) conducted at the Tacoma copper smelter, departments were identified within the plant for which both mean area air arsenic data ( $\mu\text{g}/\text{m}^3$ ) and geometric mean urinary total

**Table 4.** Summary of studies relating occupational arsenic exposure to arsenic values in urine

Occupational setting	Airborne arsenic ( $\mu\text{g}/\text{m}^3$ )	Equation relating urinary and air values	Predicted urinary As at 10 $\mu\text{g}/\text{m}^3$	Reference
Copper smelter	$n = 24$ Mean = 53 Range 3–295	$y = \left( \frac{x}{0.304} \right)$	33 $\mu\text{g}/\text{l}^a$	(12)
Copper smelter	$n = 82$ Low = 3.6; high = 52.7 Range <LOD–1,000 $\mu\text{g}/\text{m}^3$	$y = 12.6 + 1.26 x^b$	25 $\mu\text{g}/\text{l}$	(13)
Copper smelter	$n = 14$ GM = 17 Range 1–194	$y = 29 + 2.0 x$	49 $\mu\text{g}/\text{g}$ creatinine	(14)
Copper smelter	$n = 28$ NA Range up to 3,400	$y = \left( \frac{x}{0.0064} \right)^{0.515}$	44 $\mu\text{g}/\text{l}^a$	(8)
Lead–acid storage battery factory	$n = 47$ NA Range <LOD–49	$y = 11.9 + 2.43 x$	36 $\mu\text{g}/\text{l}^a$	(35)
Sulfuric acid chemical factory	$n = 18$ NA Range 6–502	$\log y = 1.098 + 0.353 \log x$	28 $\mu\text{g}/\text{g}$ creatinine	(16)
Copper smelter and arsenic trioxide refinery	$n = 24$ Smelter Mean = 12.1 Range 1.3–45 Refinery Mean = 6.9 Range 1.4–38	$y = 26 + 0.855 x$	35 $\mu\text{g}/\text{g}$ creatinine	(17)
Maintenance outage in a coal-fired power plant	$n = 40$ Mean = 48.3 Range 0.2–375	$y = 12.2 + 0.10 x$	13 $\mu\text{g}/\text{g}$ creatinine	Present study

Abbreviations:  $n$ , number of subjects studied; LOD, limit of detection; GM, geometric mean; NA, not available; MMA, monomethylarsonic acid; DMA, dimethylarsinic acid. Equations are of the general form  $y$  = urinary arsenic concentration ( $\mu\text{g}/\text{l}$  or  $\mu\text{g}/\text{g}$  creatinine) and  $x$  = air arsenic time-weighted average concentration ( $\mu\text{g}/\text{m}^3$ ). Where available, equations using urinary data for 16-hr postexposure were included in the table.

<sup>a</sup>Urinary arsenic was not speciated; values were expressed as  $\mu\text{g}/\text{l}$  total arsenic. All other urinary values in the table are expressed as the sum of arsenic metabolites (i.e.,  $\Sigma$ As metabolites or As<sub>i</sub> + MMA + DMA). Urinary concentration units are those used by the original authors.

<sup>b</sup>Linear equation derived from grouped data, Tables 1 and 2. Subjects wore chemical cartridge respirators.

arsenic data ( $\mu\text{g}/\text{l}$ ) were available from past surveys. Prior to 1971, only area air samples were collected. Regression of arithmetic mean air data on geometric mean urinary data for the 28 pairs of data identified resulted in a nonlinear relationship:  $y$  (air concentration) = 0.0064 (arsenic urine concentration)<sup>1.942</sup>. This approach is different from the usual procedure in which the measured air concentration is assigned as the fixed variable  $x$ , with  $y$  (urine concentration) as the outcome variable. (Pairs of arsenic air and urine values apparently did not relate to a single individual worker but to a departmental work area.) This relationship was then used to estimate air concentrations for the remainder of the cohort, amounting to about 2,800 men. As shown in Table 4, rearranging this equation and with a given air exposure of 10  $\mu\text{g}/\text{m}^3$ , 44  $\mu\text{g}$  As/l is predicted to be excreted in urine. The authors compared their results with those of Pinto et al. (12) and speculated that, at low air arsenic concentrations ( $\leq 300 \mu\text{g}/\text{m}^3$ ), the relationship between air arsenic and urinary

arsenic was probably poor due to interference from dietary arsenic and analytical problems. From recent data, however, it appears that for breathing zone values ranging between about 1  $\mu\text{g}/\text{m}^3$  and 1000  $\mu\text{g}/\text{m}^3$ , the relationship between mean air arsenic concentration and mean urinary arsenic concentration is very likely linear. Also, area air samples (as were principally used in this study) can misrepresent exposure when compared with data from personal breathing zone air samples collected in the same work setting (17).

Dietary interference, presumably from consumption of seafood containing DMA, was noted by Hakala and Pyy (17) in spite of speciation of urinary metabolites. Recent reports indicate that some types of seafood (e.g., mussels) may contain DMA, which can interfere with specific attribution of urinary arsenic species to airborne exposure to inorganic arsenic (17,37–39). In this present study of exposure to arsenic in coal fly ash, a dietary seafood source of arsenic is highly unlikely (Table 2). It can reason-

ably be concluded that urinary DMA concentrations observed in this study arose as a result of exposure to arsenic in the work setting as opposed to dietary sources.

The relationship between arsenic air concentrations and  $\Sigma$ As metabolites in urine in the present study of exposure to arsenic in coal fly ash (Fig. 2 and Table 4) indicates a relatively shallow slope over the range of mean exposures from 0.17 to 375.2  $\mu\text{g As}/\text{m}^3$  observed. The intercept—at about 12  $\mu\text{g As/g creatinine}$  in urine—is very similar, however, to previous studies in which dietary seafood contribution of arsenic to urinary excretion was similarly unlikely (Table 4) (13,16,35). The predicted mean  $\Sigma$ As urinary metabolites of about 33  $\mu\text{g As/g urinary creatinine}$  excreted for an air arsenic exposure of 10  $\mu\text{g}/\text{m}^3$  in copper smelters and other settings (Table 4) is nearly three times higher than that of the predicted urinary value of 13  $\mu\text{g As/g creatinine}$  observed in this study for the same TWA air exposure to arsenic present in coal fly ash dust. Taken as a whole, these observations suggest that bioavailability of arsenic from airborne coal fly ash (as indicated by urinary excretion) may be considerably less than that for a similar airborne concentration to arsenic trioxide vapors and dusts, as well as arsine gas.

Unlike other studies where  $\text{As}_3$  was shown to correlate with increasing exposure (16,17), the level of  $\text{As}_3$  was not significantly related to exposure in this study. MMA showed a very slight increase with exposure, and DMA and  $\Sigma$ As showed the strongest positive relationship with exposure. Indications from studies in animals (40–42) and humans (43–45) are that saturation or inhibition of the second step of methylation occurs at high exposures, which may lead to observations of a slight increase in MMA in urine relative to DMA. No differences were observed in the proportions of urinary MMA and DMA excreted between the highest and lowest exposure groups in this study.

Contemporary analytical work using the Laser Mass Microprobe Analyzer (LAMMA; Leybold-Heraeus, GmbH, Köln, Germany) combined with standard analytical methods has shown that the predominant arsenic compound present in coal fly ash dusts from the Novak power plant is calcium arsenate (pentavalent arsenic form) (46). The compound was found to be distributed rather uniformly on the irregular surface of fly ash particles. In contrast, the predominant arsenic compound present in the copper smelter work setting is known to be arsenic trioxide (trivalent), present as vapors and dusts. The vapor pressure of arsenic trioxide at ambient temperature is significant at about 0.6  $\text{g}/\text{m}^3$  at 25°C (47).

Smith et al. (13) collected fractionated particulate personal breathing zone samples on a subset of workers and explored correlations between individual breathing zone particle fractions termed respirable ( $<5 \mu\text{m}$ ) and irrespirable ( $>5 \mu\text{m}$ ) and urinary excretion of metabolite species. These investigators found that urinary excretion of trivalent  $\text{As}_3$ , MMA, and DMA was more closely related to exposure to irrespirable particles, that excretion of pentavalent  $\text{As}_5$  was equally related to both respirable and irrespirable particulates, and that the  $\Sigma$ As metabolites were more related to respirable than irrespirable particulates. The bulk of particles present in this power plant boiler maintenance work setting are irrespirable (Table 3); however, a portion of large particles can be deposited in the upper airways and be absorbed or coughed up and swallowed, as was also speculated by Smith et al. (13). It is likely that urinary arsenic values observed here relate predominantly to respiratory deposition of the finer particle fractions that constituted a relatively small portion of particle mass in this work setting.

In addition to exposure to arsenic dusts, exposures to arsenic vapors occur in copper smelters as well as in sulfuric acid chemical factory work settings (14,16,17). The principal exposure in the lead–acid storage battery factory was to arsine gas, with very much less exposure to arsenic particulates (35). Exposure to arsenic gases or vapors was not observed to occur in the power plant boiler maintenance work setting (20).

Differences in arsenic compound characteristics, matrix configuration and composition, and particle size distribution all probably contribute to differences in deposition, uptake, and absorption of airborne arsenic and ultimate urinary excretion in these very different workplace settings. These factors need to be carefully considered, especially when assessing results of biological monitoring for metals in different work settings (48).

## Summary

In published studies from copper smelters and other work settings, the mean of  $\Sigma$ As urinary metabolites of about 33  $\mu\text{g As/g creatinine}$  is quite consistently predicted for an air arsenic TWA exposure of 10  $\mu\text{g}/\text{m}^3$ . This level of excretion is nearly three times higher than the predicted urinary value observed in this study of coal fly ash exposures for the same TWA air exposure of 10  $\mu\text{g}/\text{m}^3$  arsenic. Results strongly suggest that bioavailability of arsenic from airborne coal fly ash (as indicated by urinary excretion) is approximately one-third of that for a similar airborne concentration to arsenic trioxide vapors and dusts as well

as arsine gas. Further detailed investigation is needed, however, to more thoroughly explore these relationships.

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